Condensation effects in *K*-shell excitation spectra of neon films

P. Wiethoff, H.-U. Ehrke, B. Kassühlke C. Keller, W. Wurth, D. Menzel, and P. Feulner

Technische Universität München, Physikdepartment E 20, 85747 Garching, Germany

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Using synchrotron radiation under high-resolution conditions, we have investigated the excitation of electronic states at the K edge in neon multilayers. In addition to the electron yield, we use photon-stimulated desorption of Ne^+, Ne^{2+}, and Ne_2^+ as near-edge x-ray-absorption fine-structure probes with different surface sensitivities. From the comparison of these signals, we obtain excitation energies for excitonic and ionic surface and bulk states. The energy of the $1s^{-1}3p$ and $1s^{-1}4p$ surface excitation is different by 0.2 eV for the p_z and the p_{xy} symmetry. The ordering of the splitting depends on the principal quantum number. [S0163-1829(97)06811-2]

Because of their structural and electronic simplicity, rare-gas solids are the ideal model systems for the study of the influence of solidification on electronic excitation and decay processes in van der Waals systems. For valence excitations, ample work on this topic has been done and collected in several comprehensive reviews.[1] For core electron excitation, results are by far less numerous, mainly because photon sources that allow investigation of core electronic states under high-resolution conditions have become available only recently. Particularly for the K-shell region of solid neon, only a few studies have been reported so far,[2–4] even though this is a very interesting sample. For example, it is well known from valence work that solid neon has a large negative electron affinity (EA), i.e., the bottom of the conduction band lies about 1 eV above the vacuum level.[1] This negative EA arises from strong short-range electron-electron repulsion, which is responsible for phenomena such as self-trapping of excitons in cavities or bubbles that form around the electronically excited particle, and the stimulated desorption of electronically excited atoms and dimers from neon films, which are expelled by those repulsive forces that are unbalanced if self-trapping occurs on the surface.[5] Even the delocalized, Bloch-like state of the free electron is only marginally more stable than a localized state, where the electron is trapped and kept inside a bubble.[6] In the bulk, the interaction of the matrix with the spatially extended distribution of the electronic wave function of excited atoms leads not only to bubble formation, but also to a compression of the Rydberg-like orbital as compared to the gas phase,[7] shifting excitation energies of bound and free-electron–hole pairs upward. Long-range polarization screening of Coulomb interactions, which would have the contrary effect and lower those excitation energies, is particularly small because of solid neon's small dielectric constant.[1] Short-range interactions that selectively probe the electronic and spatial symmetry around the excited entity are expected to dominate all shifts encountered upon solidification. The spectroscopy of $1s$ core excitons, which are strongly localized, allows the investigation of the molecular aspects of these processes, including a comparison with calculations by molecule-based techniques. Moreover, $1s$ excitation spectra of the neon atom are simple. The initial hole state is a singlet and all excitation resonances have the same symmetry $1s^{-1}np^{+1}$, $n \geq 3$.[2,8] We

therefore have investigated excitations of resonant and non-resonant $1s^{-1}$ states in solid neon and compare our results with previous work on neon in the solid state,[2,3] clusters,[4] and the gas phase.[8,9] Utilizing probes of different surface sensitivity, we are able to discriminate bulk and surface features, to detect surface symmetry breaking, and to demonstrate the existence of polarization-dependent energy shifts in core resonant excitation of surface atoms.

All data have been obtained employing the PM 5 (previously denoted HE PGM III) beam line at BESSY, Berlin, with a spectral resolution of 300 meV at the neon K edge. Excitation spectra have been recorded by monitoring either the yield of decay electrons or the yield of ions whose desorption was stimulated by electronic processes. For electrons, we used a simple partial electron yield (PEY) detector assembled from two grids (serving as adjustable high pass) and a large area electron multiplier. Desorbing ions were mass selected and recorded with a quadrupole mass spectrometer. The UHV chamber (base pressure better than 10^{-8} Pa) allowed an independent setting of the angles of polarization (surface normal against the **E** vector of the light) and detection (surface normal against the detector axis) by simultaneously rotating the detector chamber and the sample manipulator. For enhanced surface sensitivity, grazing incidence of the synchrotron light by 7° with respect to the surface was used.[10] We condensed the neon multilayers onto the (001) surface of a ruthenium single crystal that was cooled to 7 K. Before dosing, the substrate was cleaned by sputtering with Ar^+ ions, repeated heating to 1450 K in 10^{-4} Pa of oxygen, and finally flashing to 1570 K. Reproducible amounts of neon (purity better than 99.99%) were dosed by a microcapillary doser onto the substrate. The thickness of the multilayers was calibrated from thermal desorption spectra by comparing the relative areas of mono- and multilayer peaks. For all measurements reported here, the samples were 50 layers thick. Excitation spectra in the Ne $1s$ core exciton region recorded with different probes for A_z light [with the **E** vector almost parallel (7°) to the surface normal **n**] are depicted in Fig. 1. The bottom trace (labeled PEY) is the yield of electrons with kinetic energy more than 500 eV; the top three spectra show the stimulated ion desorption yield for different ions as indicated. Two different exciton series, surface and bulk, are clearly discernible and have been marked in the figure.
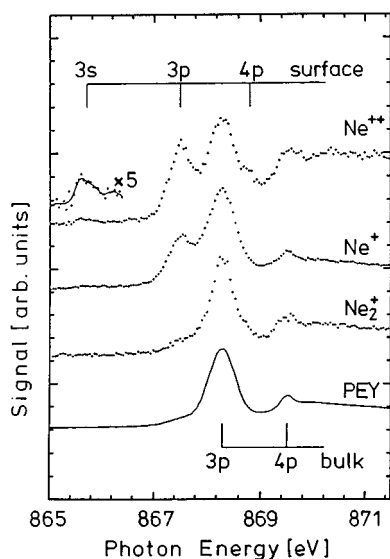
FIG. 1. Resonant neon $1s$ excitation spectra recorded with probes of different surface sensitivities, using A_z polarization. The energetic positions of bulk and surface excitations are indicated. Surface features are strongly enhanced in the photon-stimulated desorption (PSD) of Ne^{2+} and Ne^+ ions, whereas the PSD of Ne_2^+ and yield spectra of decay electrons are dominated by bulk processes.

The bulk contribution dominates the PEY and Ne_2^+ signals, whereas the surface part is strongly enhanced for the Ne^{2+} yield. The low surface sensitivity of the electron signal is due to the large mean free path of the autoionization electrons that have a primary kinetic energy more than 700 eV. The dimer ions stem from the creation and desorption of biexcitons by electrons as a secondary process.[11–13] Their signal reproduces the electron yield, with some enhanced weighting of the low-energy part of the distribution. Singly and doubly charged atomic ions, however, are created and desorbed by primary photon stimulated processes. Because of a short escape depth, which is especially short for the doubly charged species that can branch to singly charged pairs,[12–14] these ions monitor excitation events in the first few layers of the film. (We have successfully applied this technique of disentangling surface and bulk processes by utilizing probes of different escape depth previously for the study of core excitations in Ar and Kr,[15] but also for the molecules ammonia and methane.[16] The results are supplementary to data from cluster work, where the transition from the isolated particle to the solid is brought about by changing the size of the cluster.[4]

The surface signals not only show the dipole-forbidden $1s \rightarrow 3s$ transition (in the Ne^{2+} signal) but also have a strong polarization dependence (Fig. 2). Whereas the positions of the bulk lines are the same for A_z and A_{xy} polarization, the surface peaks are shifted by up to 0.2 eV for different polarizations. The $1s^{-1}3p$ energy is lower for A_z than for A_{xy}, whereas for the $1s^{-1}4p$ excitation the ordering is reversed. The $1s^{-1}3s$ transition, which is dipole forbidden in the bulk, is visible only for A_z light.

The bulk signal is in perfect agreement with data from Ref. 2, though better resolved. An extended scan reproduced the same double excitation and final-state features of solid
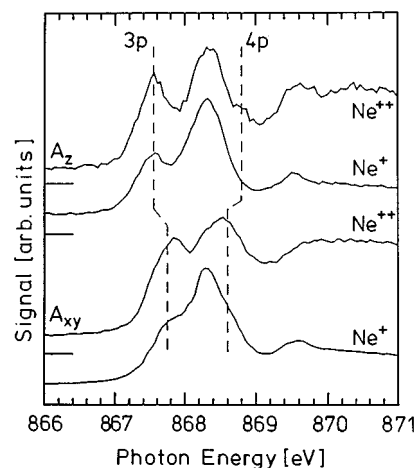

FIG. 2. Resonant neon $1s$ excitation monitored by the stimulated desorption of Ne^+ and Ne^{2+} ions. For the surface excitons, polarization shifts are obtained (see Table I).

neon that were measured in Ref. 2. In particular, the final-state effects that have been calculated in Ref. 3 were identical for $1s$ and $2s$ excitation, as expected for identical symmetry of the initial state. We therefore refrain from displaying spectra for Ne $2s$ excitation, since the rich structure due to double excitation visible in an extended $2s$ near-edge x-ray-absorption fine-structure (NEXAFS) scan has been published previously.[13]

All excitation energies are compiled in Table I. The line position of the $1s^{-1}5p$ exciton and the surface ionization edge are taken from a high-resolution threshold electron study that will be discussed elsewhere.[17] The value for the K edge in the bulk, i.e., the inner ionization potential or the energy necessary to create a free electron in the solid, is calculated from x-ray photoemission spectroscopy binding energies[12] and data from Ref. 17.

Focusing on the data in Table I, we find in going from gas to surface to bulk the following. (i) The neon $1s$ ionization potential changes. It is nearly identical for the gas and the bulk, but decreased by 1 eV for the surface. (ii) The excitation and binding energies of excitons change as well. The binding energies for the bulk and the surface are smaller than for the gas; the bulk excitation energies are larger. (iii) A dipole forbidden transition appears in the signals of the surface sensitive probes. It obviously occurs exclusively in the first layer and remains dipole forbidden for the bulk, as it is for the isolated atom. (iv) The excitation energies of the surface peaks depend upon the polarization direction. Compared with the gas-phase values, we encounter shifts in either direction, depending on quantum numbers, when the polarization of the **E** vector is changed by 90°.

Our excitation energies for the bulk excitons are in perfect agreement not only with previous values on solid neon[2] (see above), but also with results for neon clusters in the limit of large cluster size.[4] The exciton binding energies agree within the experimental uncertainty of the photon energy with values measured for the Ne $2s$ exciton series.[13,18] As discussed in Ref. 19 and pointed out in the introduction of the present paper, a combination of short-range correlation and long-range screening accounts for the energetic shifts of the bulk excitons. Screening enlarges the spatial extension of the

TABLE I. Excitation (E_{ex}) and exciton binding energies (E_b) for neon K-edge excitation. The binding energies of the surface excitons that are set in parentheses are calculated with the ionization potential of the $1s$ orbital referred to the vacuum level.

Neon K-shell excitations: Assignment and energetics (eV)							
Sample	Polarization		$1s^{-1}3s$	$1s^{-1}3p$	$1s^{-1}4p$	$1s^{-1}5p$	$1s^{-1}$
gas phase		E_{ex}	865.1[b]	867.1[a]	868.68[a]	869.25[a]	870.1[b]
		E_b	5.0	3.0	1.42	0.85	
surface	A_z	E_{ex}	865.6	867.6	868.8		869.4±0.2[c]
		E_b	(3.8)	(1.8)	(0.6)		
	A_{xy}	E_{ex}		867.8	868.6		
		E_b		(1.6)	(0.8)		
bulk		E_{ex}		868.3	869.5	869.9[c]	879.4±0.2[c]
		E_b		2.1	0.9	0.5	

[a]Reference 8.
[b]Reference 9, footnote 20.
[c]Reference 17.

Rydberg orbitals, whereas the short-range effects tend to compress them. The situation is by far less clear in the region of the surface. As yet, no calculations exist that correctly model this regime. Keeping the data of Table I in view and comparing them with cluster results, we will attempt to speculate about the microscopic details.

The ordering of the ionization potentials for the gas, surface, and bulk clearly reflects the environment dependent interaction. On the surface, the electron is able to escape to the vacuum level, i.e., final-state energies are identical for the gas and the surface. The interaction of the hole and the electron, however, is screened in the latter case, lowering the ionization potential. This screening certainly will be composed of a short-range contribution from the relaxation of the wave functions of neighboring atoms, and from long-range effects. This decrease encountered upon going from a gas to a surface environment is overcompensated in the surface-to-bulk step by the repulsion ''felt'' by the free electron inside the solid.

Repulsion is also felt by the wave functions of the core excitons, so their excitation energies are increased with respect to the gas phase. Federman *et al.*[4] have shown in cluster experiments that no continuous transition exists from the surface to the bulk species. Bulk core excitons were found only for clusters larger than some critical size, corresponding to one shell for the $3p$ exciton and two shells for the $4p$ exciton. This reflects the extension of the respective wave functions.

On the surface, these forces are asymmetric and the wave functions are distorted with respect to the almost spherical symmetry inside the fcc lattice. As a result, the dipole-forbidden $1s^{-1}3s$ exciton appears, indicating an admixture of p character to the $3s$ orbital. The transition is only seen for A_z light, indicating an admixture of only p_z character, as expected for that symmetry. We note that the corresponding signal is much larger in our data than in those of Ref. 4, due to the well-defined orientation of the **E** vector with respect to the surface normal possible in our experiment. We found a similar effect for the surface excitations of solid methane, which is isoelectronic to neon.[16] Its lowest neutral excitation C $1s \rightarrow 3a_1$, which corresponds to the Ne $1s \rightarrow 3s$ transition,

is seen for the free molecule only in transitions involving vibronic coupling (see references in Ref. 16). On the surface of condensed methane, however, the $v=0 \rightarrow v=0$ transition appears due to the distortion of the *electronic* part of the wave function by the reduced symmetry. As the $1s^{-1}3s$ exciton in neon, it is only seen with A_z light.[16]

The appearance of polarization-induced shifts of the surface exciton energies is another manifestation of symmetry breaking. Again, the amount of splitting (0.2 eV; see Table I) is comparable to that obtained for methane if we consider its $2t_2$ orbital as the analog of the neon $3p$.[16] Interestingly, the splitting is also of identical sign, the A_z transitions being lower in energy in both cases. This is surprising because the methane does not exhibit negative electron affinity like neon,[17] and one would expect the electron-electron repulsion to be weaker than for solid neon. The shapes of the NEXAFS trace envelopes for the C $1s$ and Ne $1s$ regions, respectively, are very similar for the two species, at least for the low-lying excitations. We believe that the latter sample the short-range interaction with the nearest neighbors. As a consequence, effects such as the amount and the polarization-dependent sign of the lifting of degeneracy on the surface are very similar. The positive electron affinity of methane would then be due to the larger polarizability of solid methane as compared with solid neon, which overrides repulsion and also leads to the much higher sublimation temperature of methane.

For neon, the excitation into the $3p_z$ final state is lower in energy than into the $3p_{xy}$ final state. For the $4p$ shell, the ordering is reversed. For clusters, where no polarization dependence can be measured, surface exciton energies correspond to those components that, in our study, have the lowest excitation energy.[4] For increasing cluster size the final $3p$ value is approached from lower energy and the $4p$ value from higher energy. Beyond a critical cluster size of $n \approx 200$, the $4p$ surface component vanishes.[4] In our data it is preserved, although its contribution is weak. Following our arguments given above, we would expect the excitation energies to be lower the more the excited orbitals are polarized out of the solid. Intuitively one would expect the p_z orbital,

which is oriented perpendicular to the surface, to be shifted downward with respect to the p_{xy} orbital. For $n=3$, this is indeed the case. This ordering would also be obtained if we switch to a two-dimensional band-structure view of the final state. Near the Γ point, where the transition occurs, the p_z orbitals form bonding and the p_{xy} orbitals antibonding combinations (neglecting spin-orbit coupling). However, the reversal of the ordering seen for $n=4$ clearly tell us that this picture cannot be applied here. Obviously, n-dependent (i.e., size dependent) distortion of the localized exciton wave function has to be considered. We think that our data show that the p_{xy} orbital oriented parallel to the surface can more strongly be polarized out of the surface avoiding repulsive constraints than the p_z counterpart, whose downward lobe always reaches deeply into the bulk, experiencing full repulsion.

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